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February 19, 2002

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the first-quarter FY 2002 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior (ETR) Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATT.html>.

Sincerely,

Frank McLarnon
Manager
BATT Program

cc: R. Sutula DOE/OAAT
R. Kirk DOE/OAAT
V. Battaglia ANL
K. Abbott DOE-Oakland

LBID-2405

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) PROGRAM

QUARTERLY REPORT

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BATT TASK 1 CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-Cost Li-Ion, High-Power Li-Ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to benchmark the performance of new materials for low-cost and high-power Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell, tested with a consistent protocol to determine capacity, energy, power, and lifetime characteristics. Components are then delivered to the PIs involved with BATT Program diagnostics. Fabrication and testing of the third baseline cell, namely Li metal/polymer/V₆O₁₃, will be carried out in BATT Program Task 3.1.

STATUS OCT. 1, 2001:

- Cell fabrication and testing equipment, procedures, and protocols are in place for studies of 12 cm² laminated-foil pouch cells at various temperatures and constant-current cycling studies.
- Gen 2 chemistry pouch cells with both Quallion and LBNL-made cathodes were cycled 160 times with <5% capacity fade, providing verification of the pouch cell process.
- The high-power baseline cell chemistry has been benchmarked in constant-current testing. Cells have been received from Hydro-Québec for the benchmarking of the high-energy baseline cell against current USABC goals.

EXPECTED STATUS SEPT. 30, 2002: The effort on the low-cost Li-ion baseline cell will be focused on LiFePO₄ cathodes, various gel electrolyte components applied to Celgard, and the evaluation of the available natural graphites. Electrode compositions will be optimized for electronic and ionic conductivity with the aid of collaborative modeling studies. Studies of cell and component performance as functions of temperature and electrolyte composition will be completed. Evaluation of new materials for the baseline cells will be underway: Li_{1.44}MnO₂ (LBNL), LiMn_{2-y}Al_yO_{4-z}S_z (LBNL), intermetallic anodes (ANL), and layered manganese-based cathodes (ANL).

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period.

MILESTONE: (a) Evaluate cycle-life and power capability of the LiFePO₄/gel with LiBF₄/natural graphite cell (December 2001). (b) Compare the several approaches to gel-electrolyte cell assembly using standard Li-ion electrodes (June 2002).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter:**

Work this quarter has focused on the low-cost baseline cell: LiFePO_4 /gel electrolyte/natural graphite. The first series of cells (10 cells total), two electrode films (one LiFePO_4 and one HQ-natural graphite) as well as LiFePO_4 powder were received from Hydro-Québec. In addition to the full cells, several LiFePO_4 /gel/Li metal and natural graphite/gel/Li metal cells were included to allow evaluation of the individual electrodes. The graphite-containing cells exhibited unacceptably high first-cycle irreversible capacity ($\text{IC} > 50\%$) in all configurations. The reasons for this are under investigation at HQ. The LiFePO_4 /Li cells were able to complete the characterization portion of the standard protocol. A maximum capacity density with the gel electrolyte of about 160 mAh/g was achieved at low rates as shown in Fig. 1. However, upon constant-current cycling the capacity faded quite rapidly. This was attributed to leakage of the cell, and the HQ design was subsequently modified. The next series of 8 cells has been received. These interim cells will contain $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes until the problems with the HQ natural graphite anode are resolved.

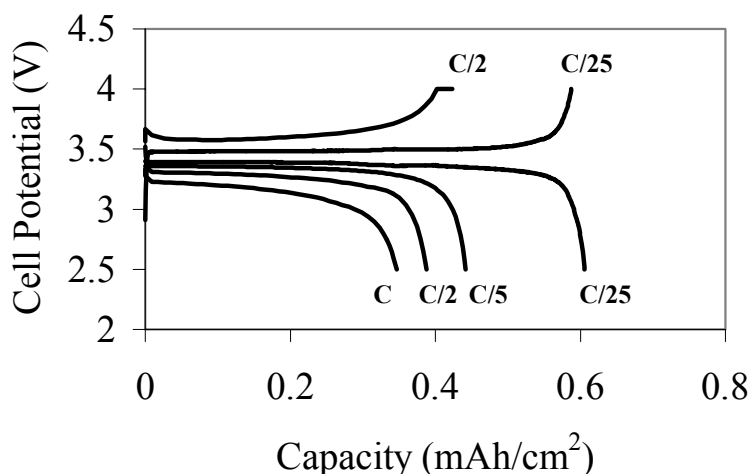


Figure 1. Performance of a LiFePO_4 /gel/Li cell at various charge and discharge rates.

The LiFePO_4 and natural graphite electrodes from HQ were studied with Celgard separator and $\text{LiBF}_4/\text{EC}/\text{DMC}$ electrolyte, both in a 1-cm^2 cell with Li-metal counter and reference electrodes and in a 12-cm^2 pouch cell. The maximum energy attained from the full cell arrangement was 32 Wh/kg because of the high irreversible capacity of the HQ graphite, as mentioned above. However, the LiFePO_4 /Li cells demonstrated capacity densities of 1 mAh/cm^2 with the higher loading electrodes. Preliminary studies of the natural graphites from Superior Graphite (SL-20, SL-25) and Mitsui Mining (coated natural graphites GDR-6, GDR-14) suggest that the SL-20 shows the lowest IC at 18 %. These will be incorporated into LiFePO_4 cells next quarter. The results from some of the candidate materials for both the low-cost and high-power baseline cell technologies will be available at the new web site after March 1 <http://issfps.lbl.gov/BattDataSite/>.

Thermally cross-linkable gel samples from Daiso and Dai-ichi gel (Japan) are being evaluated. Polymer precursor components are mixed into the electrolyte. These cross-linking conditions are studied in a glass-plate cell. Conductivity measurements are used to determine optimal time/temperature conditions. In the next quarter, optimal compositions will be added to our high-energy test pouches prepared with the well-characterized LiCoO_2 and synthetic graphite electrodes from Quallion Corp.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

SYSTEMS: Li/Polymer, Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes, inadequate capacity.

OBJECTIVES: Support cell development through structural characterization of active electrode components before, during, and after cycling. Investigate inexpensive, self-actuating overcharge protection mechanisms. Synthesize and evaluate alternative electrode materials.

APPROACH: *Subtask 1.* Address primary causes of capacity and power fading by correlating them with the composition and structure of electrode active materials using x-ray diffraction (XRD), vibrational spectroscopy, and voltammetry. *Subtask 2.* Develop internal overcharge protection mechanism that becomes active when needed and allows continued, undegraded cycling of unaffected cells. *Subtask 3.* Develop improved cathode materials *via* a rational approach to active material synthesis.

STATUS OCT. 1, 2001: The stability of LiFePO_4 at extreme potentials and states of charge has been established. Capacity fading in LiFePO_4 due to overcharging has been shown to be due to loss of active material rather than to phase conversion. New phosphate-stabilized cathode materials with high lithium content were prepared and characterized.

EXPECTED STATUS SEPT. 30, 2002: Phase transformations and accumulation of decomposition products in cycled electrodes from Task 1.1 will be identified and correlated with cell performance characteristics. The ability of electroactive polymers to provide overcharge protection will be evaluated. Potentially useful new low-cost, high-capacity electrode materials will be synthesized and tested.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Determine phase transformations in cycled cathode materials selected for use in BATT Cell development tasks (April 2002). Determine switching characteristics of electroactive conducting polymer (June 2002). Prepare and characterize novel stabilized Fe and/or Mn cathode materials (August 2002).

PROGRESS TOWARD MILESTONES

● Accomplishments toward milestones over last quarter

Subtask 1. Discharged positive electrodes removed from cycled cells Q54 and PG13 were supplied by K. Striebel. Cell Q54 had exhibited a 13% capacity loss (C/2 rate). PG13 (cycled at 60°C) had 65% loss. X-ray diffraction patterns of these cathodes showed no evidence for degradation of the active material or accumulation of new solid phases. In both cases, however, the cells were incompletely discharged; *i.e.*, the lithium content x in $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ was less than 1 after discharging. It has been reported [I. Saadoune and C. Delmas, *J. Solid State Chem.* **136**, 8 (1998).] that the cell parameters a and c of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ vary in an approximately linear manner for $0.5 < x < 1.0$. To determine the Li content in the cycled Gen 2 electrodes, $\text{Li}_{0.5}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ was prepared by chemical oxidation of Gen 2 powder by reaction with NO_2PF_6 in acetonitrile. The data for the standards and the cycled electrodes are shown in Fig. 1.

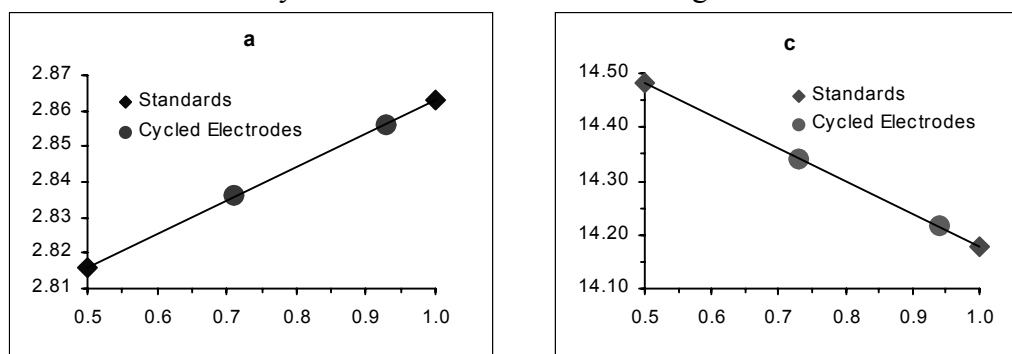


Figure 1. Lattice parameters of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ vs. x .

For sample Q54, the state of charge is about 13%. For PG13, it is about 56%. These values are consistent with a reduction of Li inventory, most probably due to electrolyte reduction at the anode.

Subtask 2. *In situ* electropolymerization of 3-methylthiophene on porous composite cathodes in Li and Li-ion cells resulted in a conducting polymer coating on the surfaces of the electrode particles. Little or no penetration of the separator occurred. Internal shorting of the cells during overcharging was therefore not achieved. Various methods of preparing separators incorporating the electroactive polymer prior to cell assembly are being examined. These include chemical oxidation of soluble precursors, electropolymerization on an inert, flat electrode, and solution deposition of soluble electroactive polymers.

Subtask 3. The transition metal fluoride phosphates prepared and characterized in FY 2001 have not shown good capacities for Li intercalation, and have been set aside. Several new mixed transition metal (Fe, Mn) phosphates based upon the sodium alluaudite structure are now under investigation. These materials are similar in stoichiometry to LiFePO_4 , but have a more complex structure, with MO_6 units sharing edges rather than corners (Fig. 2). In contrast to LiFePO_4 , they have better electronic conductivity, support high intercalant ion mobility, and allow changes in metal oxidation states without undergoing first-order phase transitions. They are also easily and rapidly prepared in air. An investigation of their electrochemical properties is under way.

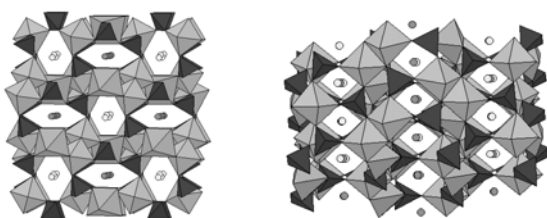


Figure 2. $\text{LiMnFe}_2(\text{PO}_4)_3$ c-axis and a-axis projections.

TASK STATUS REPORT

PI, INSTITUTION: K. Zaghib, Hydro-Québec Research Institute

TASK TITLE - PROJECT: Cell Development - Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIER: High cost of Li-ion batteries

OBJECTIVES: (a) To fabricate Li-ion polymer cells (4 cm² area) using cell chemistries proposed by DOE. Cells (50% of total) will be sent to LBNL for testing. (b) To investigate phenomena at the anode/separator and cathode/separator interfaces. (c) To determine the cycle life of Li-ion polymer cells at different temperatures (55 to 0°C) and self-discharge rates. (d) To synthesize LiFePO₄ cathode material for Li-ion polymer cells.

We want to determine the effects of: (1) LiFePO₄ particle size, (2) the amount of conductive carbon in the electrodes, (3) the mixed salt concentration (from 1 M to 2 M), on battery performance.

APPROACH: Our approach is to synthesize and prepare electrodes (anode and cathode) with low-cost materials for evaluation in Li-ion polymer cells containing gel polymer electrolytes. The effect of LiFePO₄ particle size, the amount of conductive carbon in the electrodes, and the salt concentration (mixed salt, from 1M to 2M) on battery performance will be investigated. The effect of pressure and interfacial phenomena on electrode performance will also be studied.

STATUS OCT. 1, 2001: We completed the coating of electrodes containing graphite, LiFePO₄ and Li₄Ti₅O₁₂ with variable capacities. Samples of these coated films were sent to LBNL for evaluation. Li-ion gel polymer cells were fabricated and testing was underway.

EXPECTED STATUS SEPT. 30, 2002: Fabricate and send additional cells to LBNL for evaluation. Complete tests to determine the effects of pressure on the performance of Li-ion polymer cells. Select suitable procedure to coat gel polymer as (i) over coating on Celgard separator or (ii) free-standing polymer electrolyte.

RELEVANT USABC GOALS: 10 year life, < 20% capacity fade over a 10-year period.

MILESTONES: Ten cells were provided to LBNL in October 2001 for evaluation. Seven extra cells have been sent to LBNL in December 2001, based on passivation-free chemistry Li₄Ti₅O₁₂/gel polymer/LiFePO₄. We expect to provide the second deliverable of ten cells by the end of January 2002. We expect to optimize the cell assembly by using a new sealing method.

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestone over last quarter**

We are continuing to study the effect of pressure (10, 20, and 30 psi) on the performance of polymer gel at the anode and cathode interfaces by impedance spectroscopy, SEM and electrochemical methods (galvanostatic). The cell configurations for this study were:

Li/gel polymer /graphite and Li/gel polymer/ LiFePO_4

The data show that pressure has a more pronounced effect at the anode interface than at the cathode interface (Fig.1).

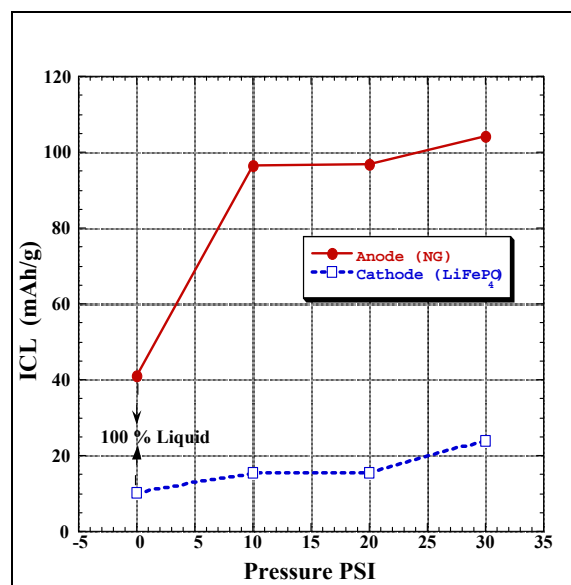


Figure 1

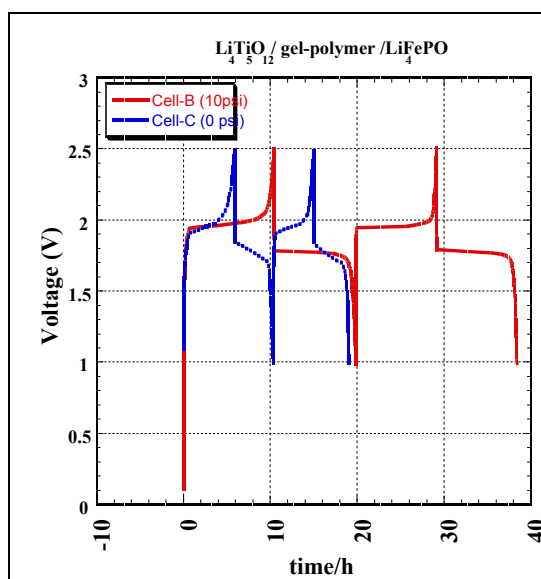


Figure 2

During this study we observed that the irreversible capacity loss (ICL) is higher by 10% in Li-ion gel cells than in cells containing a liquid electrolyte. In order to eliminate the influence of the ICL, we investigated a baseline chemistry of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /gel/ LiFePO_4 , which should not form passive films on the electrodes.

The results of the irreversible and reversible capacities are shown in Fig. 2. It appears that a pressure of 10 psi is necessary to obtain good reversible capacity. Even with a passivation-free anode, the reversible capacity is lower by 50% compared to a cell under 10 psi pressure.

Seven extra cells with this configuration were delivered to LBNL in December 2001 for evaluation.

- Further plans to meet or exceed milestones:** We have started testing new family of gel polymer electrolyte cross linked by electron beam (EB) radiation at LTEE (Shawinigan) facilities. Ten cells with this gel polymer will be assembled and sent to LBNL by the end of January 2002.

- Reason for changes from original milestones:** N/A

BATT TASK 2 ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-cost Li-ion

BARRIER: Cost and safety limitations of Li-ion batteries.

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and that provide capacities >400 mAh/g and >1000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The task entails the synthesis and electrochemical evaluation of the intermetallic electrodes and their structural characterization by X-ray diffraction and spectroscopy. The reactivity of the intermetallic electrodes with the electrolyte will be determined by calorimetric techniques.

STATUS OCT. 1, 2001: We identified intermetallic compounds with various structure types that convert to lithiated zinc-blende-type structures during reversible electrochemical reactions. Cu_6Sn_5 , InSb , and Cu_2Sb have formed the basis for our studies. Cu_2Sb yielded the best electrochemical performance and stability. Against a Li electrode, Cu_2Sb delivered a stable capacity of ~ 300 mAh/g, which translates to 1914 mAh/ml, for at least 25 cycles. These novel intermetallic electrodes, which operate by a reversible Li insertion/metal extrusion reaction with an invariant metal host subarray, provided a new approach for the design of alternative anode materials with acceptable capacity, performance, and stability.

EXPECTED STATUS SEPT. 30, 2002: We expect to increase the cycle life of intermetallic electrodes based on tin and antimony to more than 100 cycles with capacities in excess of 300 mAh/g and 2000 mAh/ml in Li half-cells (K. Striebel). Through collaborative efforts, we will have studied the nature of the electrode/electrolyte interface and obtained data on the thermal stability of the intermetallic electrodes with respect to the electrolytes. Detailed structure/electrochemical property relationships will have been obtained primarily by XANES, EXAFS, and XRD studies at the Advanced Photon Source at Argonne and by HRTEM imaging.

RELEVANT USABC GOALS: 10-year life, $<20\%$ fade over a 10-year period.

MILESTONES: Our primary milestone will be to achieve a reversible electrochemical capacity of tin and/or antimony based intermetallic electrodes in excess of 300 mAh/g and 2000 mAh/ml for more than 100 cycles by April 2002. Efforts to understand structure/electrochemical property relationships, electrode/electrolyte interfaces, and thermal stability of the intermetallic electrodes will be on-going through September 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Intermetallic electrodes tend, in general, to show an unacceptably large irreversible capacity loss (30-40%) on the first cycle. Therefore, efforts have been made in this past quarter to understand the reasons for this capacity loss, particularly for Cu_2Sb , in order to devise methods to combat this effect. Several factors that could be responsible for capacity loss were investigated: 1) an oxide passivation coating on the surface of the Cu_2Sb electrode, 2) a large electrode particle size that might cause particle disintegration and current collection problems, 3) electrode porosity that is lost when the copper is extruded from the Cu_2Sb crystals, and 4) copper diffusion away from the electrode particle surface that prevents the re-incorporation of all the extruded copper.

1) Oxide passivation coating. Cu_2Sb was synthesized by various methods: (i) by high-energy ball milling (HEBM), (ii) by melting the sample as an ingot under inert atmosphere, (iii) by treating a HEBM sample with hydrogen, and (iv) by a solution-precipitation method. Samples made by HEBM had the highest oxygen content and those made by the solution precipitation method, the second highest. Methods (ii) and (iii) were found to yield Cu_2Sb products with a very low oxygen content. Some of the irreversible capacity loss that was detected above 1.4 V vs. Li was determined to be due to the electrochemical reduction of the oxide coating. However, in most cells, this is only 1-2% of the total capacity delivered on the first discharge. Samples made from a melt or those that had been treated under hydrogen did not show this extra capacity.

2) Particle size effects. Cu_2Sb samples were treated under hydrogen (4%) and sieved to various particle sizes. Although the impedance on the first cycle appeared to be greater for samples with a larger particle size, the electrochemical reaction, which involves a Li insertion and Cu extrusion process, quickly pulverizes the individual particles, thereby discounting particle size as a major factor for the capacity loss effects.

3) Electrode porosity. Because Cu is extruded from Cu_2Sb during the electrochemical reaction, it could decrease the porosity of the electrode significantly, and limit the access of electrolyte to the active particles. This phenomenon could, therefore, affect the electrochemical capacity of the Cu_2Sb electrode, particularly if all the extruded copper is not reincorporated back into the structure during the reverse reaction. Cu_2Sb electrodes with 35% and 80% internal porosity were made and cycled. Although no significant difference in capacity was observed during the first 2-3 cycles, the electrodes with lower porosity performed better over time.

4) Excess copper. In an attempt to compensate for any extruded Cu, which loses electrical contact with the lithiated antimonide host electrode during the initial reaction, Cu_2Sb electrodes (30-35% porous) were fabricated with 10-18% excess Cu. Although excellent coulombic efficiency was obtained from these cells, there was only a marginal improvement in the initial irreversible capacity (29%) in some of the cells.

Cycle life tests of Li/ Cu_2Sb cells are being continued but, at present, their performance (250 mAh/g) falls short of the 300mAh/g goal that has been set for 2002. A study of Mn_2Sb , which is isostructural with Cu_2Sb , has been initiated to complement the evaluation of Cu_2Sb electrodes.

- **Further plans to meet or exceed milestones:** None.
- **Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-cost Li-ion battery and gel battery

BARRIER: Cost, safety and volumetric capacity limitations of Li-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte. In particular we will investigate manganese-tolerant anode materials.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2001: We determined that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure aluminum was found to have a high capacity and it reacted readily with Li, but its capacity faded rapidly upon cycling in carbonate-based electrolytes. Several simple binary alloys of Al showed an even higher capacity fade than Al itself. Tin-containing materials, such as MnSn_2 appeared to cycle well for a few cycles, before capacity fade set in.

EXPECTED STATUS SEPT. 30, 2002: We expect to identify several additional non-Al binary alloys, to improve the electrochemical performance of the materials identified, and to design a program to understand and remediate capacity fade upon cycling.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone is to identify by September 2002 a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 volts relative to pure Li. In addition, we will design a program to identify, understand and mitigate the capacity loss during cycling of simple alloy systems.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

As agreed in the AOP we are now generating a plan to build a better understanding of the capacity loss in simple binary metal systems, particularly for carbonate based electrolyte systems. One example is MnSn_2 , which cycles well for a few cycles then decays rapidly. There is a complete reaction (turnover) of the tin of about five before degradation sets in, indicating that the compound is inherently reversible.

We will grow thin alternating films of tin and manganese, collaborating with Professor E. Cotts, then measure their interdiffusion to form tin-manganese compounds and determine electrochemical behavior as a function of film composition and particle size. We will also determine changes in microstructure as the Li is cycled, and the impact of oxygen species on particle stability.

We will compare this system with the Sn-Mo-O system which has been reported to cycle well both as an oxide (Morales et al) and as thin metal films (Dahn et al). This system, although possibly too heavy for practical application, will act as a promising reference point; because in the oxide, the Sn and Mo appear to be mutually soluble, in the metal films mixed alloys are present.

There is a large effort at Binghamton investigating lead-free solders for electronics packaging applications. We are working with them on their tin-based solders that might possibly lead to attractive tin-based anode materials; we reported on one such material last quarter.

- **Further plans to meet or exceed milestones:** None.
- **Reason for changes from original milestones:** N/A

Presentation

S. Yang, Y. Song, P. Y. Zavalij and M. S. Whittingham, "Nanocomposite Electrodes for Advanced Batteries," *Materials Research Society National Meeting*, Boston, MA, Nov. 28, 2001.

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and M.D. Curtis, University of Michigan

TASK TITLE – PROJECT: Anodes - Novel Composite Anode for Lithium-ion Batteries

SYSTEMS: Low-cost Li-ion

BARRIER: Safety, irreversible capacity loss, and self-discharge

OBJECTIVES: The primary objective is to improve the overall safety, cycle life, and shelf life of the Li-ion battery through the development of a novel composite anode with no irreversible capacity loss during initial cycles, and with high energy and power density.

APPROACH: Our approach is to develop composite anode through prelithiation to remove the irreversible capacity loss and provide high performance anode with thermal and chemical stability for application in large size Li batteries. The composite anode will be engineered to be compatible with the existing Li-ion chemistry. The composite anode also provides a new opportunity to construct Li cells using lower cost and stable electrolytes.

STATUS OCT. 1, 2001: We have proposed to develop a composite anode with no irreversible capacity loss and with superior gravimetric and volumetric energy density. Further, this new composite anode will provide a new opportunity to be used in combination with high energy and high rate non-lithiated cathodes that will allow the use of much lower cost electrolytes (PC-based electrolytes). While the focus of our work will be on the development of composite anode, during 2001, we have also developed a Li-phosphonate polymer that is stable in the operational voltage range of carbonaceous anodes with the added benefit of expected fire retardant properties. Also, a unique, *in situ* technique was developed for exploring the reactivity of anode/electrolyte interfaces.

EXPECTED STATUS SEPT. 30, 2002: A novel composite anode with no irreversible capacity loss will be delivered for application in large size Li-ion batteries. The main focus will be on optimization of rate capability, energy density, and safety aspects of the composite anode. The novel process to be developed in this work is applicable to alternative anodes such as carbonaceous anodes, oxides, nitrides, and phosphides systems. Further, the electrode impedance will be minimized for application in high power batteries.

RELEVANT USABC GOALS: Improved safety of Li ion batteries, long cycle and shelf life, compatibility for high power batteries, and new opportunity to develop practical battery for HEVs and EVs.

MILESTONES: Preparation and evaluation of optimized composite anodes with no irreversible capacity loss; 6/15/2002:

We have investigated the possibility of using chemical prelithiation of oxides and nitride anodes. Our preliminary results indicate that our process can transform the oxide anode to metallic state, ready for further formation of reversible lithium alloys. Characterization of the composite anode indicates that the anodes consist of nano-cluster of metals stabilized within a lithium oxide matrix (in the case of oxide), and in the lithium nitride (in the case of metal nitride).

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have developed a chemical process to produce composite anodes with high gravimetric and volumetric energy density with no irreversible capacity loss. While the process is general, we have applied the process to oxide and nitride anodes. Preliminary results indicate that metal oxides and nitride can be reduced to metallic state, ready for lithium-alloy formation. The X-ray diffraction and TEM analysis of the composite anode indicate formation of metal clusters stabilized by lithium oxide in the case of oxide anode and stabilized with lithium nitride in the case of nitride anode.

We have further proceed to over-lithiated the reduced oxides and nitrides, and our preliminary results indicate the possibility of forming stable lithium alloys within the composite matrix. This over lithiation process has provided a new opportunity to use the non-lithiated cathodes (*i.e.*, V_6O_{13}) to make totally a new Li cell consists of high energy density anode and high energy density cathode. The composite anode has been charged and discharged in half- cells and provide almost no irreversible capacity loss for the first cycle. Test of the composite anode, which is over-lithaited to form lithium alloy against vanadium oxide cathode, is in progress.

- **Further plans to meet or exceed milestones:**

We have established the possibility to prepare composite anode with no irreversible capacity loss. Now we are planning to optimize the chemical process to prepare composite anode with tunable Li content. Plan is also in progress for further scale-up of the process to prepare the composite anodes. We will report our detail observations of the process and cell performances during DOE review at LBNL in July 2002.

- **Reason for changes from original milestones.**

Due to the urgent need to develop alternative anodes for large size batteries with high safety margin, high energy, and high power density, we have initiated a new process to make composite anode through a low cost chemical process to remove the large irreversible capacity loss of the oxide and nitride anodes. Preliminary results are encouraging and this new process may provide anodes with significantly higher energy and power density. The new composite anode using our novel process also may improve the safety aspects of large size Li-ion cells and batteries.

BATT TASK 3 ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities due to instability to 4-V.

OBJECTIVES:

- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (*e.g.*, 4 V) and develop materials and methods to increase stability.

APPROACH: A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

STATUS OCT. 1, 2001: A study of the effects of polymer electrolyte properties on dendrite growth at Li metal electrodes was completed. Polymer electrolytes were prepared that are designed to define the upper limits of ion transport for polymer electrolytes (conductivity $>10^{-4}$ S/cm, $D_s >10^{-8}$ cm²s⁻¹ and $t^0_+ >0.3$ at 20°C with LiTFSI). An initial survey of the effect of polymer structure on stability toward high voltage was initiated. Lab cell (1cm²) testing of the Li/polymer system was established and baseline data sets completed.

EXPECTED STATUS SEPT. 30, 2002: Quantitative measurements of the primary factors involved in dendrite growth will be completed (transport and mechanical properties). Transport and mechanical properties will be measured for less costly salts (LiTf, LiPF₆ and LiBF₄) and the cost vs. performance will be assessed. Lithium/polymer and gel-polymer cell testing at an appropriate larger cell size (*e.g.*, 25 or 100cm² area) will be established and compared with Lab cell performance. Diagnostics will be developed to characterize electrolyte/binder changes that cause increase of ASI and capacity fade.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

MILESTONES:

1. Electrolyte properties that inhibit dendrites measured quantitatively (09/30/02)
2. Complete scale-up for Li/polymer and gel polymer cell construction and testing (03/31/ 02).
3. Establish correlations between large scale and lab cell performance (09/30/02).

PROGRESS TOWARD MILESTONES

1. Accomplishments toward milestone over last quarter: Cycling of symmetrical Li/polymer electrolyte /Li cells and Li/uncross-linked polymer electrolyte/ V_6O_{13} cells has been carried on the 1 cm^2 electrode area scale. Electrolytes that have been examined are: PEO-LiTFSI; PEO-LiTFSI; comb branch polymers $PEPE_3$ -LiTFSI and $PEP(TMO)_3$ -LiTFSI and linear cross-linkable PEO, polyoxetane and poly(EOTMO) all with LiTFSI. (TMO stands for trimethylene links between the ether oxygens and EO for ethylene links). Some cells have been successfully built with reference electrodes to allow examination of the impedance of the individual electrodes (25% successful). Lithium figure of merit (Li_{FOM}) testing has also been carried out with Li/polymer electrolyte/stainless steel cells. This measurement provides a measure of the Li cycling efficiency and the tendency to form mossy Li deposits. Presently Li_{FOM} values greater than 10 have been achieved although in prior work with PEO-LiTFSI a Li_{FOM} of 150 was measured. The electrolytes have been analyzed for side reaction products and the comb-branch materials show fragmentation that is consistent with the side chain structure.

Dendrite growth appears to depend upon salt concentration in a complicated fashion. Dendrites appeared rapidly when Li was cycled with a PEO-LiTFSI electrolyte with an O:Li ratio of 8:1. No dendrite formation was observed for hundreds of cycles with a concentration of 30:1. These results indicate that depletion of Li ions at the charging electrode is not the cause but that phase changes at the discharging electrode due to salt concentration increases plays a significant role. Salt concentration effects are also observed to play a significant role in the development of the ASI in cycling Li/ V_6O_{13} cells.

Transport property measurements of $PEP(TMO)_3$ -LiTFSI electrolytes have been made. Conductivity is significantly higher at low temperatures ($<20^\circ\text{C}$) for the TMO structures than EO polymers but the same for higher temperatures. This effect is clearly related to the glass transition temperatures (T_g). The T_g -values for EO polymers rise from -65 to 0°C as the LiTFSI content is increased from zero to 5:1 ratio. The increase for the TMO polymer is only from -75 to -55°C for a similar concentration increase. This implies that the TMO polymers will have much better low-temperature conductivity and interfacial behavior. Salt diffusion coefficients were measured to be only $3 \times 10^{-8}\text{ cm}^2/\text{s}$ at 85°C but only decreased to $10^{-8}\text{ cm}^2/\text{s}$ at 25°C . PEO-type polymers range from 8×10^{-8} to $10^{-8}\text{ cm}^2/\text{s}$ for the temperature range 85 - 40°C . Initial impedance measurements also indicate lower interfacial impedances with these polymers.

- **Further plans to meet or exceed milestones:** Preparation and testing of cross-linked polymer electrolytes will be carried out and modification of the Li surface will be studied to reduce the interfacial impedance. Transference numbers for the TMO polymers will be obtained.

2. Accomplishments toward milestone over last quarter: Completion of this milestone has been postponed three months due delays in arrival of new staff. It is not expected that this delay will affect completion of either milestone 1 or 3. Large batches (100g) of pre-polymer have been prepared and the structures of the cross-linking units have been varied to allow the mechanical properties to be tuned. Larger scale syntheses (500 g) of monomers have been successful with distinctly improved monomers. These stockpiles of materials are ready for use in membrane formation studies in both Li/polymer and Li-ion gel cell systems. Completion of these studies will allow an appropriate scale-up and completion of milestone 3.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer

BARRIER: Short lithium battery lifetimes and high costs.

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We intend to correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data to be collected include modulus, ionic conductivity, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2001: We established that fumed silica-based composite electrolytes with low-molecular weight PEOs exhibit conductivities exceeding 10^{-3} S/cm at 25°C and have electrochemical properties (Li transference number, conductivity) decoupled from mechanical properties, thus providing a range of mechanical modulus (as high as 10^9 Pa). We determined that fumed silica stabilizes the Li/electrolyte interface effectively suppresses Li dendrite growth, and significantly improves cycle performance and electrochemical efficiency. We also observed that different surface groups present on the silica effect varied improvement on electrochemical performance in both half- and full-cell studies with a V_6O_{13} cathode. Fumed silica A200 having 100% hydrophilic silanol surface groups exhibits better electrochemical performance than R805 having 48% hydrophobic octyl surface groups.

EXPECTED STATUS SEPT. 30, 2002: Using the baseline high-molecular weight PEO + LiTFSI system, we expect to determine the effect of fumed silica on conductivity and electrolyte/lithium interfacial stability and how these results vary with type of fumed silica surface group.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES:

1. Develop protocols for incorporating varying amount of fumed silica with a variety of surface chemistries (*e.g.*, -OH, octyl-, and crosslinkable moieties) into LBNL baseline polymer electrolytes. (March 2002)
2. Complete Li/CPE/Li and full-cell cycling studies using 3-V vanadium oxide cathodes with composites developed from milestone 1. (September 2002)
3. Acquire rheological data for materials generated from milestone 1 for correlation with electrochemical stability. (September 2002)

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

We were in a transition period last quarter, changing our focus from the low-MW oligomeric PEO (PEG-dm) to the baseline high-MW PEO ($MW = 2 \times 10^5$). In this regard, we have developed a procedure to prepare the polymer electrolyte film and have compared room-temperature conductivities measured in a coin cell with those measured in a more conventional glass conductivity cell. The results agree with each other.

We have preliminary rheological results for high-molecular weight PEO. For example, a composite of 10 wt% A200 fumed silica in high-MW PEO exhibits solid-like behavior at 80°C, which is above the melting point of PEO. This ability of fumed silica to produce a mechanically strong network structure might be exploited to extend the use temperature of PEO-based electrolytes.

We are using conductivity measurements as a tool to develop protocols for incorporating fumed silica in base-line materials (Milestone 1). We also have preliminary conductivity results for high-MW PEO + LiTFSI + fumed silica (10 wt%) systems: (1) in $P(EO)_{10}LiTFSI$ (O:Li=10) electrolyte, the conductivity at temperatures from 15 to 90°C decreases with addition of hydrophilic A200 or hydrophobic R805 fumed silica, which agrees with recent results of Shriver and coworkers (*J. Phys.Chem. B* **2001**, *105*, 9016); (2) in $(PEO)_{20}LiTFSI$ system, the conductivities at temperatures from 15 to 50°C increase with the addition of the fumed silica but above 50°C decrease; and, (3) the conductivities of $P(EO)_{10}LiTFSI$ are greater than those of $(PEO)_{20}LiTFSI$. The preliminary results indicate that adding fumed silica increases the conductivity when the polymer electrolytes are crystalline but decreases conductivity when the polymer electrolytes are amorphous. Although the mechanism of this action is not yet clear, it seems that the state of polymer crystallinity plays an important role.

The preliminary results also suggest that solid low-MW PEO in conjunction with fumed silica might be used to obtain mechanical properties similar to the high-MW material while maintaining desirable conductivity at room (or slightly higher) temperature.

Further plans to meet or exceed milestone: We continue to study effects on conductivity of fumed silica surface groups, amount of fumed silica and Li salt, and PEO molecular weight. We will design and construct a new temperature bath system for use in full-cell cycling studies above ambient conditions.

•Reason for changes from original milestone: N/A

TASK STATUS REPORT

PI, INSTITUTION: D. DesMarteau and S. Creager, Clemson University

TASK TITLE - PROJECT: Electrolytes - New Battery Electrolytes based on Oligomeric Lithium bis((perfluoroalkyl)sulfonyl)imide Salts

SYSTEMS: Li/polymer

BARRIER: Short Li battery lifetime. Low Li battery power density.

OBJECTIVES: (1) Develop methods for synthesizing oligomeric ionene lithium salts based on the bis((perfluoroalkyl)-sulfonyl)imide anion. (2) Develop methods for preparing solid polymer electrolytes (SPEs) from the target salts. (3) Provide data on the ionic conductivity and lithium transference of the target SPEs at variable temperature and composition. We expect these studies will lend insight into the effects of anion size, chain length, and linker structure on SPE ionic conductivity and lithium transference.

APPROACH: Salts will be synthesized using methodologies developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem.* 1995, **72**, 203-208). SPEs will be prepared from crosslinked low-MW polyethylene glycol (PEG) and also non-crosslinked PEG for comparison. Conductivities will be measured using electrochemical impedance spectroscopy.

STATUS OCT. 1, 2001: Contract was signed to initiate project in late Jan. 2002.

EXPECTED STATUS SEPT. 30, 2002: Dimeric salts with different perfluorinated chains linking sulfonyl imide anion groups together, and oligomeric ionene salts utilizing the same linkers in longer chains, will have been synthesized. SPEs from the salts will have been fabricated in polyether matrices, and their ionic conductivities measured at various temperatures and compositions. A method for measuring Li^+ transference based on DC potentiostatic polarization is being implemented, and progress in measuring Li^+ transference in the target SPEs will have been made.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over 10 year period, 1000 cycles.

MILESTONE: Our two major project milestones are as follows:

1. Synthesize new ionene lithium salts based on oligomeric bis((perfluoroalkyl)sulfonyl)imide anion structures.
2. Characterize the electrical properties of polyether-based solid polymer electrolytes from the target salts at variable temperature and salt content.

Progress toward the milestones will be ongoing as new salts are synthesized and are made available for characterization. Synthetic and characterization work on dimeric Li salts should be completed by Sept 30, 2002. Synthesis and characterization of oligomeric salts should be started and preliminary results obtained by Sept 30, 2002.

PROGRESS TOWARD MILESTONES

Contract was signed and in place in late January 2002. Two graduate students and one undergraduate student are working on the project.

TASK STATUS REPORT

PI, INSTITUTION: D.F. Shriver, S. Vaynman, Northwestern University

TASK TITLE - PROJECT: Electrolytes - Highly Conductive Polyelectrolyte-Containing Rigid Polymers

SYSTEMS: Li/polymer

BARRIER: Low ionic conductivity of the polymer electrolyte, electrochemical instability of the polymer electrolyte toward Li electrodes.

OBJECTIVES: The primary objective is to synthesize and test a new class of highly ionically conductive, rigid polymer electrolytes for rechargeable Li batteries.

APPROACH: Our approach is to modify the highly ion-conductive rigid polymer electrolytes previously synthesized at Northwestern University by replacing electrochemically unstable carboxy groups with more inert oxygen-rich functional groups such as sulfones, thus increasing the stability of the electrolyte toward Li electrode. At least two polymer-salt complexes will be synthesized, and their properties will be measured. These electrolytes will be tested in Li batteries.

STATUS OCT. 1, 2001: We synthesized highly conductive rigid polymer electrolytes that contain functional groups such as carboxy and sulfone and tested them in cells. Polymer-salt complexes that contain carboxy groups have high ionic conductivity (ca. 10^{-4} S/cm at room temperature), but are unstable toward Li. The ionic conductivity of three recently synthesized polysulfone-salt complexes is lower. One of the polymer electrolytes had ionic conductivity at room temperature approaching 10^{-4} S/cm. The stability toward Li of polymer-salt complexes that contain sulfone groups is much higher than that of polymer-salt complexes that contain carboxy groups.

EXPECTED STATUS SEPT. 30, 2002: This project will terminate on May 31, 2002. During the remaining four months we will synthesize promising polymer(s) in larger quantity, test their stability toward Li metal, and also test them in cells. We will prepare a final report that summarizes this research.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are:

1. To synthesize and test promising polymer systems by 4/2002 with the goal of conductivity higher than 10^{-4} S/cm at room temperature. The stability toward battery components should be high; the resistivity of the Li/polymer electrolyte cell should not increase more than a factor of two during the first week.
2. To prepare a final report by 5/31/2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:**

Our project focused on:

- a. chemical synthesis of highly ion-conductive rigid polymer electrolytes,
- b. study of the ion-transport properties of these electrolytes,
- c. investigation of interactions at the Li electrode/polymer electrolyte interface,
- d. testing the electrolyte in a battery configuration.

During the last quarter we continued synthesis and investigation of the properties of polysulfones (a), (b) and (c) (Fig. 1). The conductivity of the polysulfone (a)-lithium triflate complex was approximately 5×10^{-6} S/cm at room temperature. This complex was much more stable toward the Li anode than the complex containing carboxy groups. Due to low ionic conductivity of electrolyte, the capacity of the cells containing the polysulfone (a) - lithium triflate polymer electrolyte was low.

The conductivity of the polysulfone (b)-lithium triflate (2:1 molecular ratio) complex was extremely low; it could not be measured at room temperature. At 60°C the conductivity was approximately 3×10^{-9} S/cm, and this may be due to the low density of cation-coordinating sites in this polysulfone.

The sulfone-containing polymer (c), which has a much higher density of cation-coordinating sites than polysulfone (a or b) was also synthesized. As expected when doped with lithium triflate in 2:1 molecular ratio, polymer (c) displayed much higher ionic conductivity (approximately 10^{-4} S/cm at room temperature) than polymers (a and b). At the present time we are in the process of synthesizing of a new batch of this polymer. When synthesized, the conductivity measurements will be repeated. This polymer-salt complex will be tested to determine the polymer's stability toward Li; if its stability is high, the complex will be tested in a battery configuration.

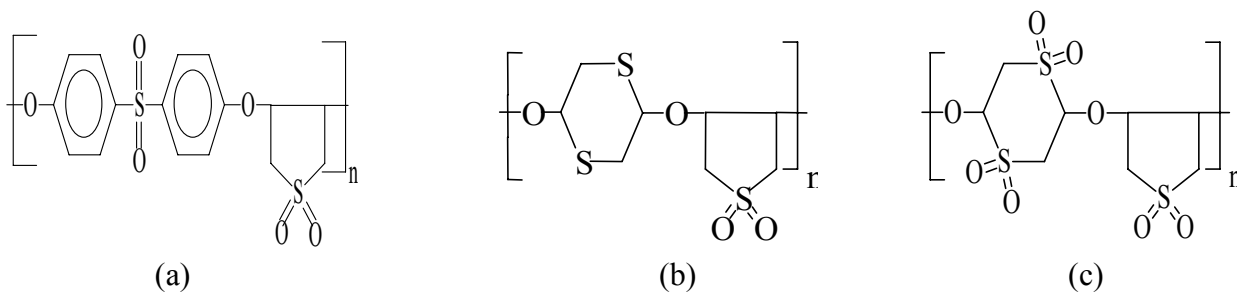


Figure 1. Structure of polysulfones under investigation.

- **Further plans to meet or exceed milestones:** We did not meet our prior milestones because a new post-doctoral fellow did not join our team until December. Now he is synthesizing polymers for further testing.

- **Reason for changes from original milestone:** The reasons for changes from the original milestones are given above. The contract runs through May 2002, and over this period of time the synthesis and testing of polymer electrolytes will continue. A final report will be prepared in May 2002.

TASK STATUS REPORT

PI, INSTITUTION: K. Kinoshita, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Electrolyte Additives

SYSTEMS: Low-cost Li-ion, high-power Li-ion

BARRIER: Safety of Li-ion batteries

OBJECTIVES: The primary objective is to identify chemical additives that improve the safety of nonaqueous electrolytes for Li-ion batteries by stabilizing the SEI layer on carbon.

APPROACH: The thermal stability of the ATD Program Gen 2 baseline electrolyte [1.2 M LiPF₆ in EC/EMC (3:7)] will be investigated by heating samples at 85°C in sealed vials. Experiments will be conducted to determine the catalytic influence of cell components such as active electrode materials from the ATD Gen 2 chemistries on the thermal stability of the baseline electrolyte. Analytical techniques will be used to detect the presence of decomposition products from electrolytes in the presence of electrode materials. Capillary electrophoresis will be used to study Li salt degradation, and GC-MS will be used to study solvent degradation. Evidence suggests that the addition of an organic base such as pyridine reduces the decomposition rate of EC/DMC by limiting the disproportionation of LiPF₆. We plan to conduct further experiments with pyridine as an electrolyte additive. TEM and AFM will be used to study the effect of additives on the thickness and structure of the SEI layer and the irreversible capacity loss on carbon electrodes. Thermal analysis studies will be used to determine the thermal stability of carbon electrodes containing SEI layers.

STATUS OCT. 1, 2001: The polyether carbonates (CH₂CH₂O)_mCOO)_n [PE₃C] were identified as possible decomposition products when 1 M LiPF₆ in 1:1 EC:DMC was heated to 85°C. The PE₃C should simulate the end product that may be produced during the formation of the SEI layer (electrolyte decomposition) at the anode. The Illinois Institute of Technology (IIT) has evaluated PE₃C as an additive in 2016 coin cells (Li/carbon) containing 1 M LiPF₆-EC-DEC and the anode from ATD Program Gen 1 cells. Electrochemical studies showed that the presence of the electrolyte additive has a very small effect on the reversible capacity but produces a higher irreversible capacity loss. The negative electrodes from these coin cells were examined by TEM. There was no obvious difference in the SEI layer that was observed on graphite removed from cells with or without PE₃C additive. Pyrrole was investigated as an electrolyte additive. The irreversible capacity loss on graphite during the formation cycle was higher when pyrrole was present, suggesting it may have no benefit as an electrolyte additive.

EXPECTED STATUS SEPT. 30, 2002: We expect to complete studies on the catalytic effect of active electrode components on the thermal stability of the ATD Gen 2 baseline electrolyte. The study of pyridine in altering the thermal stability of the ATD Gen 2 baseline electrolyte will be completed

RELEVANT USABC GOALS: Identify additives that improve the safety of Li-ion batteries.

MILESTONES: Complete analysis of the thermal stability of 1.2 M LiPF₆ in EC/EMC (3:7) containing pyridine as an electrolyte (3/02).

PROGRESS TOWARD MILESTONES

The effects of additives on the electrochemical behavior of Gen2 carbon electrodes have been studied. Pyridine and vinylene carbonate have been examined. The pyridine has been studied with LP-40 electrolyte (EC:DMC (1:1)-LiPF₆ (1M)) and with EC:DMC-LiClO₄(1M) electrolyte in order to evaluate the effects of the LiPF₆ salt. It has been shown that pyridine can intercept the reactive PF₅ Lewis acid that initiates ring opening of the EC and leads to polymer formation and gas generation. It is apparent from voltammetry and impedance measurements that the pyridine is also reduced on the anode and forms a different layer than the electrolyte alone. The film formed in the presence of LiPF₆ apparently generates more impedance than the film formed in the presence of LiClO₄. This may be due to the formation of the pyridine-PF₅ adduct that facilitates reduction to a passivating film. The competing effects of bulk-phase reactions of the additives with electrode reactions leads to a complex situation that is difficult to analyze. Further chemical analysis of the products formed is necessary before definite conclusions may be drawn. However, the effect of the additive on full cell behavior must be determined before too much effort is expended on surface analysis.

A plausible mechanism for CO₂ generation that also provides a rationale for CO generation and reversible and irreversible self-discharge of Li-ion batteries has been developed. The ring-opening polymerization of EC is thought to generate polyether carbonates that decompose to CO₂ and PEO-like polymers. This reaction may be catalyzed by acids (PF₅) or bases (formed by reduction of solvent at the anode). The polymeric material leads to decreased ion transport in the composite electrodes and consequent fading of power and energy densities. The proposed mechanism is being tested by a number of studies of the electrolyte stabilities when contacted by the electrode components and by simple thermal treatment. The analytical facilities for this are under development.

Removal of EC from the electrolyte is recommended but it is usually required for intercalation with the carbonaceous anode. Vinylene carbonate has been reported to provide useful effects at carbonaceous electrodes that eliminate the need for EC. The electrochemical and chemical behavior of this material is also under study.

TASK STATUS REPORT

PI, INSTITUTION: J. Prakash, Illinois Institute of Technology

TASK TITLE - PROJECT: Electrolytes - Nonflammable Electrolytes and Thermal Characterization

SYSTEMS: Li-ion cells

BARRIER: Thermal safety

OBJECTIVES: The goal of this proposal is to assist DOE/BATT in developing advanced high-performance Li-ion cells for electric and hybrid vehicles. The objectives of this project are: (1) to develop nonflammable electrolytes with high flash point ($>100^{\circ}\text{C}$), ionic conductivity (10^{-3} S/cm), and wider voltage window (0-5 V vs. Li); and (2) to carry out thermal investigations of the flame-retardant (FR) additives in Li-ion cells.

APPROACH: Our research approach will include (1) the development of thermally stable and nonflammable electrolytes to provide safety and (2) thermal diagnostic studies of the Li-ion cells using differential scanning calorimetry (DSC) and accelerated rate calorimetry (ARC) in order to understand the degradation, failure, and safety mechanisms.

STATUS OCT. 1, 2001: We completed the synthesis of the FR hexa-methoxy-tri-aza-phosphazene $\text{N}_3\text{P}_3 [\text{OCH}_3]_6$ and supplied this material to ANL for further testing in PNGV Li-ion cells. We also completed the mechanistic studies of the interaction of the HMTAP with the anode in Li-ion cells and observed the existence of the $\text{Li-P}(\text{OCH}_3)_2$ species on the electrode surface.

EXPECTED STATUS SEPT. 30, 2002: This project is being discontinued and we expect to conclude the project by the end of September 2002. During this period, we will complete the electrochemical and thermal characterization of the FR additive HETAP in Li-ion cells using DSC and ARC. We will also complete the mechanistic studies of the FR additive HETAP in Li-ion cells in order to understand the catalytic reaction of the FR additive with the electrode/electrolyte during the requested extension of this project.

RELEVANT USABC GOALS: Thermal and fire safety of the EV batteries under normal and abusive conditions.

MILESTONES: The electrochemical, thermal, and mechanistic studies of the new flame retardant HETAP in Li-ion cells will be completed by the end of September 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:**

1. During last quarter, we completed the synthesis of the flame retardant (HETAP) and characterized this additive for its structure and purity. The synthesis was carried out by dissolving hexachlorocyclotriphosphazatriene (5 g, 0.0575 mole) in pyridine (21 ml) followed by the addition of ethanol (16 ml). The temperature was maintained at 0-5°C during the addition and the reaction mixture was stored overnight. Diethyl ether (100 ml) was then added in this mixture with stirring, and the pyridinium chloride was removed by filtration. Subsequent distillations produced hexa-ethoxy-cyclotri-phosphazatriene (yield =52%). The FT-IR spectra confirmed the molecular structure of the HETAP synthesized. The FT-IR spectra of the synthesized HETP compound exhibited two strong absorptions at 2980 and 2934 cm^{-1} (asymmetric stretching of the $-\text{CH}_2$ and $-\text{CH}_3$ groups), absorption at 2877 and 2819 cm^{-1} (symmetric stretching of the $-\text{CH}_2$ and $-\text{CH}_3$ groups), and absorption at 1388 and 1364 cm^{-1} (symmetric and asymmetric bending frequency of the ethyl groups). The stretching of P-N and P=N group was also observed at 1213, and 750 cm^{-1} . Strong absorption bands at 1262, 1097 cm^{-1} indicated the presence of symmetric and asymmetric stretching of P-O-C group.

2. Cyclic voltammetry was used to investigate the oxidative stability of the HETAP additive in (EC+DMC)/LiPF₆ electrolyte. The cyclic voltammograms were obtained on a glassy carbon disk electrode between 2.0 and 5.0 V (see Fig. 1). Comparable electrochemical stability was observed for both the electrolytes containing 0 wt% and 5 wt% HETAP additive suggesting that the HETAP additive is electrochemically stable up to 4.5 V vs. Li. Further studies are currently in progress.

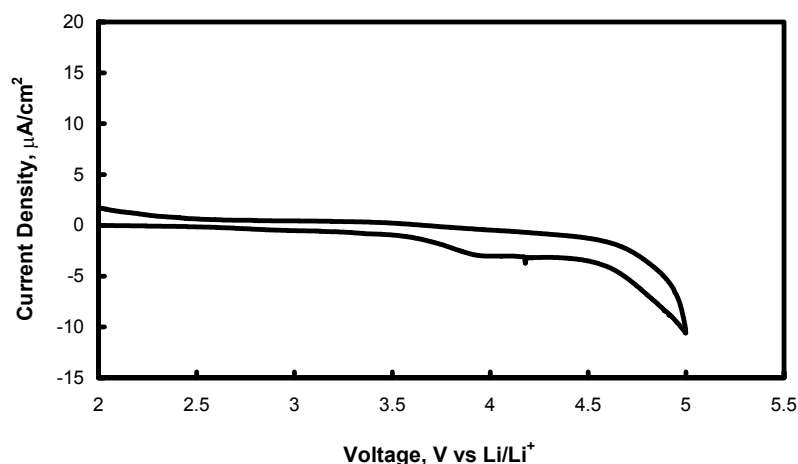


Figure 1. Cyclic voltammogram of a glassy carbon electrode in EC-DMC/1 M LiPF₆ electrolyte containing 5-wt% HETAP.

- **Further plans to meet or exceed milestone:** We plan to complete the electrochemical and thermal performance of the HETAP in Li-ion cells and the mechanistic investigations on HETAP in order to understand the catalytic reaction of the FR additive with the electrode/electrolyte, especially at higher temperatures, by September 2002.

BATT TASK 4 CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Low-cost (Li-ion) battery and Li-polymer battery

BARRIER: Cost limitations of Li-ion and Li-polymer batteries

OBJECTIVES: To develop low-cost manganese-oxide cathodes to replace vanadium oxide electrodes in Li-polymer cells and cobalt electrodes in Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes that can be used in Li-ion and Li-polymer cells; the electrodes will be synthesized in the discharged and charged states, respectively. For Li-ion cells, focus will be placed on layered lithium-manganese oxide structures that do not convert to spinel during electrochemical cycling, particularly those stabilized by a Li_2MnO_3 component, and those with a $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$ composition ($\text{M}=\text{Ni}, \text{Co}$); for Li-polymer cells. The electrode material of choice is stabilized $\alpha\text{-MnO}_2$.

STATUS OCT. 1, 2001: We exploited the concept of using a Li_2MnO_3 component to stabilize layered LiMO_2 structures with the ultimate objective of stabilizing layered LiMnO_2 . In particular, we expanded our synthesis efforts to include solid solutions of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ compositions, where $\text{M} = \text{Mn}, \text{Ni}, \text{or Co}$, or a combination thereof. To date, these materials have yielded specific capacities of approximately 150 mAh/g between 4.5 and 3.0 V in Li half-cells at 50°C, but for less than 100 cycles. Studies of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ compositions were initiated in which $\text{M}' = \text{Ti}, \text{Zr}$, *i.e.*, with $\text{Li}_2\text{M}'\text{O}_3$ components that are isostructural with Li_2MnO_3 .

EXPECTED STATUS SEPT. 30, 2002: Improvements in the electrochemical performance of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ electrodes will have been achieved with a targeted goal of 160 mAh/g for 100 cycles at 50 °C in Li-ion cells. Layered $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$ compounds ($\text{M}=\text{Ni}, \text{Co}$), in particular $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ that yield 150 mAh/g for 50 cycles at 50 °C in Li-ion cells will have been synthesized. Stabilized $\alpha\text{-MnO}_2$ electrodes for Li-polymer cells will have been evaluated in collaboration with LBNL (J. Kerr); the targeted performance of these electrodes is 200 mAh/g for 100 cycles at 80°C. A detailed understanding of the structural/electrochemical property relationships in the above-mentioned electrode systems will have been gathered by a variety of techniques such as XRD, XANES, EXAFS, NMR, and HRTEM.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: (a) Synthesize and evaluate $\text{LiMn}_{1-x}\text{M}_x\text{O}_2$ compounds ($\text{M}=\text{Ni}, \text{Co}$) (April 2002); (b) achieve a technical target of 150 mAh/g for 50 cycles at 50 °C (June 2002); (c) achieve the targeted milestones for the performance of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ electrodes in Li-ion cells and for stabilized $\alpha\text{-MnO}_2$ electrodes in Li-polymer cells (September 2002).

PROGRESS TOWARD MILESTONES

- Accomplishments toward milestones over last quarter:** Work this past quarter focused on synthesizing and electrochemically characterizing a standard $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode and a series of $x\text{Li}_2\text{TiO}_3 \cdot (1-x)\text{LiMn}_{1-y}\text{Ni}_y\text{O}_2$ composite electrodes, in which $0 \leq x \leq 0.1$, and $y=0.5$. The electrodes have layered structures in which the oxygen array shows trigonal symmetry (Fig. 1). These electrode materials have compositions that fall within the Li_2TiO_3 - $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ - $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ phase diagram (see previous reports).

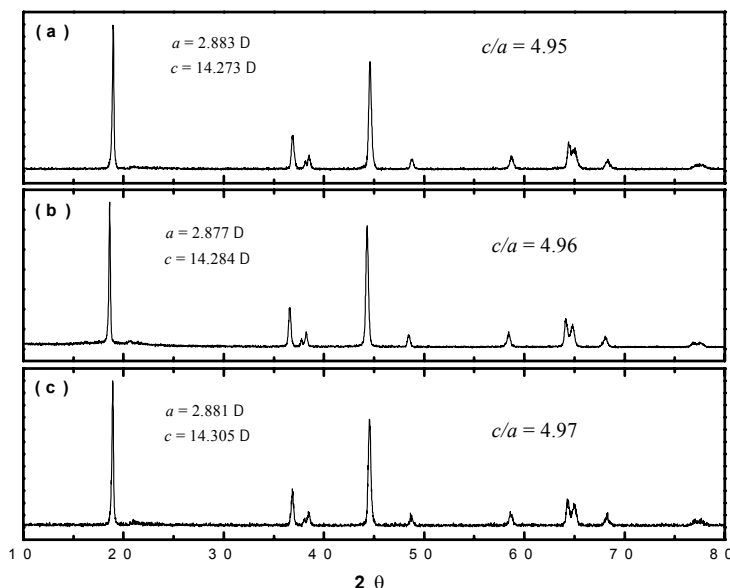


Figure 1. XRD patterns of $x\text{Li}_2\text{TiO}_3 \cdot (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes for a) $x=0$; b) $x=0.05$; c) $x=0.1$.

The research groups of Ohzuku and Dahn have recently evaluated the electrochemical properties of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$. We have confirmed their data and have achieved a rechargeable capacity of more than 140 mAh/g at room temperature for 50 cycles. These electrodes show a large irreversible capacity drop on the first cycle when charged and discharged between 4.6 and 2.5 V. We have attempted to decrease the irreversible capacity loss by using $x\text{Li}_2\text{TiO}_3 \cdot (1-x)\text{LiMn}_{1-y}\text{Ni}_y\text{O}_2$ composite electrodes in which the electrochemically inactive Li_2TiO_3 component has relatively strong Ti-O bonds compared to Mn-O and Ni-O bonds. Although $0.05\text{Li}_2\text{TiO}_3 \cdot 0.95\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes deliver 160 mAh/g for more than 50 cycles at 50°C between 4.6 to 2.5 V vs. a Li counter electrode, the irreversible capacity loss on the first cycle was not significantly improved. However, at room temperature, the coulombic efficiency of a $0.05\text{Li}_2\text{TiO}_3 \cdot 0.95\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode stabilizes at 99.5% compared to 97.7% for the standard $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode. Cyclic voltammetry data, which show a marked decrease in the oxidation potential of a $0.05\text{Li}_2\text{TiO}_3 \cdot 0.95\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode vs. Li during the first three cycles before stabilizing at 3.95 V, suggest that the superior coulombic efficiency of $\text{Li}/0.05\text{Li}_2\text{TiO}_3 \cdot 0.95\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cells may be attributed to a decrease in the oxygen activity at the surface of delithiated electrode particles at high states of charge. From the voltage profile, there is no indication of spinel formation during electrochemical cycling. Future work will focus on improving the performance of these electrodes.

- Further plans to meet or exceed milestones:** None
- Reason for changes from original milestones:** N/A

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/polymer/gel and low-cost Li-ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized and characterized, both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2001: We determined that layered manganese dioxides can be structurally stabilized, that their stability is a function of current density and/or cut-off voltages, that their electronic conductivity can be significantly enhanced, that their cell cycling can be substantially improved by addition of other transition metals, and that hydrothermally synthesized manganese oxides cycle as well as high-temperature materials. We also showed that vanadium oxides can also be stabilized by the addition of manganese ions, and that lithium iron phosphate can be synthesized very rapidly in a hydrothermal reactor.

- Layered $\text{Li}_x\text{Co}_y\text{Mn}_{1-y}\text{O}_2$: ≥ 200 Ah/kg for 8 cycles, and stabilized $\text{Li}_x\text{MnO}_2 \geq 150$ Ah/kg for 6 cycles
- Layered $\text{Mn}_{0.1}\text{V}_2\text{O}_5$; ≥ 200 Ah/kg for 6 cycles.

EXPECTED STATUS SEPT. 30, 2002: For low-cost Li-ion cells, we expect to identify the changes in LiMnO_2 structure as a function of current density in cell cycling, to determine the structure and composition of the vanadium stabilized LiMnO_2 and to increase its electrochemical capacity. For Li/polymer cells we expect to complete the evaluation of the manganese stabilized δ -vanadium oxides and to compare them to the iron phosphates. Emphasis in all cases will be placed on understanding the reasons for capacity fade. We will also have determined the feasibility of using a hydrothermal approach to the manufacture of lithium iron phosphate.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones this year are: (a) to characterize the pillared manganese oxide, and improve its capacity to 150mAh/g with an ultimate goal of 200 Ah/kg, (b) complete the characterization of manganese stabilized vanadium oxides and (c) to compare the best samples with iron phosphates for polymer or gel batteries by July 2002.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestones over last quarter:

(a) Stabilized Manganese Oxide Cathodes

We are exploring the phase stability region of the vanadium pillared layered manganese dioxides to find a material that has higher capacity at high discharge rates. A hollandite phase (2 x 2 tunnels) competes with the layer phase under most synthetic conditions, and we are characterizing and performing electrochemical evaluation on both phases now.

We have prepared carbon-coated samples of the stabilized layer phase, $\text{Li}_{1+x}\text{Ni}_y\text{Co}_z\text{Mn}_{1-x-y-z}\text{O}_2$. These samples show good rate capability even at room temperature, as indicated in the figure below, where 50% capacity is utilized even at 3 mA/cm^2 . Thus, 1st cycle capacity is 150, 140, and 95 mAh/g at 0.5, 0.83 and 3 mA/cm^2 respectively.

(b) Stabilized Vanadium Oxide and Iron Phosphate Cathodes

We have completed the exploration of the hydrothermal method as a low-cost manufacturing process for lithium iron phosphate. The hydrothermal material is not the same as the high temperature material, but converts to it during the carbon coating process. However, the iron atoms are still partially disordered leading to material of lower quality than that formed by firing the reagents at an elevated temperature, either in the presence or absence of carbonaceous species. We will thus use the iron phosphate formed at elevated temperatures as a comparison standard for our new cathode program.

Crystalline iron phosphate has been formed, characterized and electrochemically evaluated. It has also been carbon coated to increase the particulate conductivity; carbon coating significantly increased the capacity allowing capacities of around to be 150 Ah/kg to be attained. We have evaluated the effect of carbon coating method on the capacity as a rate of discharge rate. Our initial data suggests that the carbon coating/addition process is not very important but that the carbon loading level is critical. 5 wt% carbon gives poor capacity, whereas 10-15% gives the same high capacity.

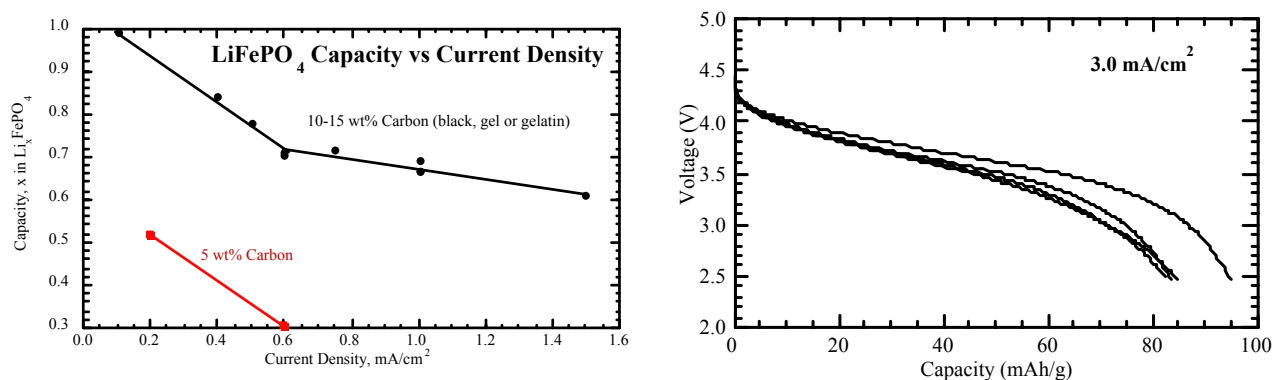


Figure 1. High-rate cycling at room temperature of carbon coated (left) LiFePO_4 and (right).

- **Further plans to meet or exceed milestones:** N/A
- **Reason for changes from original milestones:** N/A

Publications: S. Yang, Y. Song, P.Y. Zavalij and M.S. Whittingham, "Reactivity, Stability and Electrochemical Behavior of Lithium Iron Phosphates," *Electrochem. Commun.*, **4** (2002) in press. M.S. Whittingham and P.Y. Zavalij, "Control of the Structure and Properties of Vanadium and Manganese Oxides through Tailored Soft Synthesis," *Int. J. Inorganic Materials*, **3** (2001) 1231-1236.

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.*, sol-gel, glycine-nitrate combustion). The microstructures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on structurally stable materials such as tunnel-containing manganese oxides, as well as those of commercial interest, such as spinels and lithium iron phosphate.

STATUS OCT. 1, 2001: A milestone to provide $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$ to the BATT program in fall 2001 was met and samples of tunnel-containing Li_xMnO_2 were also provided. Several synthetic approaches for producing LiFePO_4 were evaluated, and sol-gel was considered the most promising.

EXPECTED STATUS SEPT. 30, 2002: Initial screening of novel P2 substituted layered manganese oxides will be completed, and a go/no go decision made based on the results. Recommendations will be made on the appropriateness of selected cathode materials for the BATT program. A design for an *in situ* x-ray diffraction cell will be finished.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:

- 1) Provide samples of conventional LiFePO_4 or sol-gel synthesized $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.97}\text{S}_{0.03}$ to the BATT program for testing (11/01): **completed**
- 2) Design *in situ* x-ray diffraction cell for structural studies of Li_xMnO_2 (6/02) literature review in progress.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

Laminated electrodes with loading levels of either 80% $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$ (12% total carbon, 8% PVdF binder) or 84% (8% total carbon, 8% binder) were tested in Li half cells (2032 coin cells). Carbon content had a marked effect on utilization (Fig. 1) and pressed electrodes cycled better on the 4V plateau (Fig. 2). Extending cycling to the 3V plateau causes a rapid capacity fade. Similar results were obtained on electrodes containing 80% “ $\text{Li}_{1.02}\text{Al}_{0.15}\text{Mn}_{1.85}\text{O}_{3.96}\text{S}_{0.04}$ ” (10% C black) provided to us by Dr. Sun, who originally reported on this material (*J. Electrochem. Soc.*, **147**, 2116 (2000)) (Fig. 3). Significantly, fading is seen when the cells are cycled on the 3 V plateau, in contrast to the original report. We believe that the apparent suppression of capacity loss observed previously is primarily a kinetic effect and cannot be sustained over prolonged cycling regimes. Details of electrode composition/fabrication and cell history determine whether or not capacity fading is seen (both at 4 V and at 3 V). Electrodes fabricated by pressing powders onto aluminum exmet (as in the original paper) may cycle better than laminates at 3 V, but are less relevant to large-scale battery production. Other disadvantages to this material are the low rate capability and reduced capacity at 4 V (~80-90 mAh/g), while the stability gained is only marginal. For these reasons, we do not plan to do further work on $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$, but will concentrate on novel layered manganese oxides, tunnel manganese oxides, LiFePO_4 , and related materials in the coming quarters.

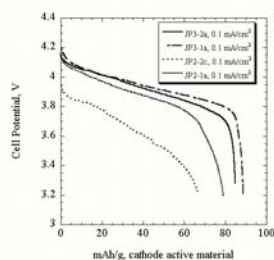


Figure 1

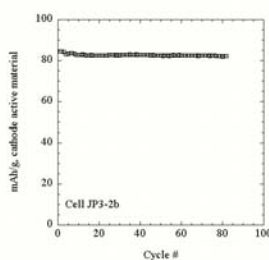


Figure 2

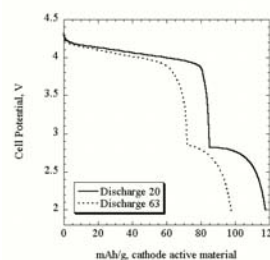


Figure 3

Figure 1. (left) Discharges at 0.1 mA/cm^2 ($\sim C/4$ rate) of Li/1M LiPF_6 , EC-DMC/ $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$ coin cells. JP3-2a and JP3-1a electrodes contain 80% active material (prepared in-house) and 12% total carbon; the latter was pressed prior to incorporation in coin cells. JP2-2c and JP2-1a electrodes contain 84% active material and 8% total carbon; the latter was pressed.

Figure 2. (middle) Capacity as a function of discharge number (0.2 mA/cm^2 , $\sim C/2.4$ rate) for cell JP3-2b, containing a cathode having 80% active material and 12% total carbon, which was pressed.

Figure 3. (right) Discharges 20 and 63 of a Li/1M LiPF_6 , EC-DMC/ $\text{Li}_{1.02}\text{Al}_{0.15}\text{Mn}_{1.85}\text{O}_{3.96}\text{S}_{0.04}$ coin cell over both the 3 and 4 V plateaus, at 0.055 mA/cm^2 ($\sim C/6$ rate). The electrode in this cell was provided to us by one of the researchers who originally synthesized and reported on $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.98}\text{S}_{0.02}$.

- **Further plans to meet or exceed milestones** N/A
- **Reason for changes from original milestones** N/A

TASK STATUS REPORT

PI, INSTITUTION: J. Evans and T. Devine, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Corrosion of Aluminum in Li Cell Electrolytes

SYSTEMS: High-power Li-ion battery

BARRIER: Limitations on cycle or “shelf” life.

OBJECTIVES: The primary objective is to quantify corrosion of aluminum when used in present or candidate Li cell electrolytes. Aluminum is a relatively inexpensive material that is widely used for the positive electrode current collector and cell containment.

APPROACH: The approach uses an electrochemical quartz crystal microbalance (EQCM) to determine the initial rates of corrosion of aluminum in BATT electrolytes as a function of potential and to discover whether passivation occurs. One of the Li salts ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$) of the three baseline chemistries has been shown to corrode aluminum in prior LBNL work. Experiments on coated aluminum samples and longer term experiments (where exposed samples are examined at the scanning electron microscope) will also be conducted. As newer electrolytes (with higher performance characteristics or minimal CO_2 venting problems) are discovered their corrosivity to aluminum will be determined.

STATUS OCT. 1, 2001: No recent work on this project.

EXPECTED STATUS SEPT. 30, 2002: EQCM/cyclic voltammetry measurements completed on pure and carbon-coated Al samples in contact with three electrolytes most relevant to the BATT Program.

RELEVANT USABC GOALS: Cycle life >500 cycles. 10-year life, <20% capacity fade over a 10-year period.

MILESTONE:

July 31: Measurements of the corrosion of aluminum in $\text{LiPF}_6 + \text{PC}:\text{EC}:\text{DMC}(1:1:3)$ completed using the EQCM.

Sept. 30: Measurements of the corrosion of aluminum in $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N} + \text{PEGDME}$ (PEO analog) completed using the EQCM.

PROGRESS TOWARD MILESTONES

Project start awaits arrival of post-doc towards end of second quarter. Milestones are delayed accordingly.

BATT TASK 5 DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: F. McLarnon and R. Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVE: Establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity/power decline.

APPROACH: Use ellipsometry, Raman spectroscopy, and advanced microscopic techniques to characterize electrodes taken from baseline BATT Program cells, as well as thin-film electrodes in model cells. Our goal is to identify changes in electrode surface morphology, electrode surface chemistry, and SEI thickness and composition, which accompany cell cycling.

STATUS OCT. 1, 2001: We defined the relationships between electrode history, electrolyte composition, electrode surface properties, and temperature for a model thin-film spinel LiMn_2O_4 cathode.

EXPECTED STATUS SEPT. 30, 2002: We identified changes in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode surface chemistry, which accompanied cycling in $\text{LiPF}_6\text{-EC-EMC}$ electrolyte, and identified surface carbon loss as a potential cell degradation mode.

RELEVANT USABC GOALS: 0 year life, < 20% capacity fade over a 10-year period.

MILESTONE: (a) Determine the effect of sulfur and aluminum additives on the structure, surface morphology and chemistry of LiMn_2O_4 electrodes (January 2002). (b) Characterize surface processes such as changes in surface morphology, chemistry, and SEI formation on LiFePO_4 and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.97}\text{S}_{0.03}$ model thin-film cathodes (June 2002).

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter:

Effect of sulfur and aluminum additives on LiMn_2O_4 electrodes: We completed our study of the effects of added S on the surface chemistry and morphology of LiMn_2O_4 electrodes during FY 2001, as reported in the BATT Program quarterly report issued in October 2001. We did not receive LiMn_2O_4 electrodes with Al additives, therefore we changed the focus of this milestone to determine the effects of Al additives on the structure, surface morphology, and chemistry of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrodes. We carried out a series of diagnostic tests on $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes taken from BATT Program baseline cells as well as the cathodes from ATD Program Gen 2 cells. We focused on detecting possible structural changes, new oxide phase formation, or phase segregation as we previously observed in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ electrodes. The results of our studies confirm that Al has a stabilizing effect on the structure of mixed Ni and Co oxides and prevents their decomposition upon cycling or storage at elevated temperatures. This result completes our January 2002 milestone.

We used Raman microscopy and current-sensing atomic force microscopy (CSAFM) to study cathodes, anodes, and separators from BATT Program baseline cells, which were assembled and tested by K. Striebel.

Raman microscopy of the composite $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode from a cell which was cycled ~300 times at 60°C revealed a loss of carbon from the cathode surface to a much greater extent than was observed in a cell cycled at room temperature (October 2001 report).

Raman maps of the cathode show the cathode components SFG-6 graphite, acetylene black, and oxide in color-coded images as green, blue and red, respectively (Fig. 1).

Interestingly, the two carbon components disappear from the cathode surface at different rates, depending on their particle size and structure; *i.e.*, the surface concentration of acetylene black decreases at a higher rate than graphite. Among possible causes of this phenomenon are carbon migration or peeling, oxide particle dissolution-deposition, new oxide phase formation, and carbon oxidation. CSAFM measurements revealed that the cathode surface electronic conductance decreases dramatically with increasing cell test temperature, which is in concert with the observed carbon loss. Moreover, we determined that the cathode surface consists of partially (and sometimes almost fully) charged $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ particles, despite deep discharges at the end of cell testing. Degradation of electronic contact between grains of active material may be responsible for this effect. We found no clear evidence of nano-crystalline deposits or non-conductive SEIs on the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode surfaces.

A new spectro-electrochemical cell was designed for *in situ* studies of thin-film electrodes. We will employ it to study surface phenomena at model sulfur-doped LiMn_2O_4 spinel and LiFePO_4 electrodes in the coming weeks.

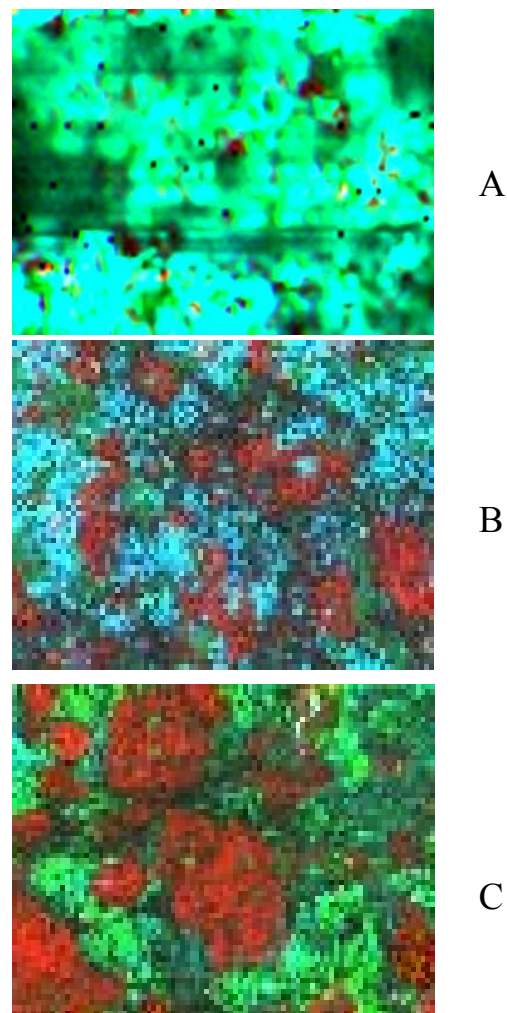


Figure 1. Raman microscopy of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes. A: fresh cathode, B: cell cycled ~300 times at room temp, C: cell cycled ~300 times at 60°C. Red: $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, green: graphite, blue: acetylene black. Images size is 40 x 60 μm .

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: High-power Li-ion, high-energy Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode materials changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM).

STATUS OCT. 1, 2001: We have completed an extensive study of the effect of Li and O stoichiometry on the phase behavior of spinel LiMn_2O_4 cathodes during cycling at ambient and at low temperatures. The effects of electrode history on the phase behavior of LiMn_2O_4 cathodes were also investigated.

EXPECTED STATUS SEPT. 30, 2002: We expect to complete our investigation of LiMn_2O_4 at 55°C. We also expect to complete our work on XAS at the P K-edge and its use in detection of electrolyte decomposition products. This will include application of the technique in the ATD Program. The cathode studies will include work on high capacity materials such as LiFePO_4 and substituted layered LiMnO_2 .

RELEVANT USABC GOALS: 15-year life, <20% capacity fade over a 10-year period.

MILESTONES: (1) Complete stability studies of LiMn_2O_4 and in LiF based electrolytes, at 55°C, by April 30, 2002. (2) Complete work on XAS at the P K-edge and apply it to materials from the ATD program by August 31, 2002. (3) Complete *in situ* XAS and XRD studies of LiFePO_4 and substituted layered LiMnO_2 by December 31, 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 over last quarter:** A paper on the effect of composition and cycling history on the stability of LiMn_2O_4 was submitted for publication. Work on stability studies of LiMn_2O_4 and in LiF based electrolytes, at 55°C , has been completed. Recent work shows that the addition of our anion complexing agents to conventional LiPF_6 based electrolytes improves cycling stability at 55°C .
- **Further plans to meet or exceed milestone:** It is anticipated that the milestones will be met on time. This will complete our work on LiMn_2O_4 spinel materials.
- **Reason for changes from original milestone:** Because of the limited energy density no work will be done on $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.97}\text{S}_{0.03}$.

- **Accomplishments toward milestone 2 over last quarter:** Techniques were developed, in the last quarter, to collect XAS data at the P K-edge in both the fluorescence and electron yield mode. This included the design and construction of an electron yield detector for use at Beam Line X19A at NSLS. Early this quarter, the setup was used to investigate phosphorous containing compounds in cathodes, anodes and separators from cycled cells from the ATD program.
- **Further plans to meet or exceed milestone:** It is anticipated that the milestones will be met on time
- **Reason for changes from original milestone:** N/A

- **Accomplishments toward milestone 3 over last quarter:** *In situ* XRD studies were done on a carbon coated Si anode material that was obtained from Prof. Yoshio of Saga University. The measurements will be repeated this quarter. Substituted layered LiMnO_2 was obtained from two sources. Preliminary *in situ* XRD data were obtained on a Ni substituted LiMnO_2 .
- **Further plans to meet or exceed milestone:** It is anticipated that the milestones will be met on time
- **Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: Low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) to study model electrode/electrolyte combinations, *e.g.*, using glassy carbon electrodes and BATT Program electrolytes, to provide the basis to interpret more-complex spectra recorded for ATD Program cell materials.

STATUS OCT. 1, 2001: Used Density Functional Theory (DFT) to calculate oxidation potentials of different Li-ion battery electrolytes and additives.

EXPECTED STATUS SEPT. 30, 2002: Together with other members of the project, establish thermal and electrochemical stability of different Li-ion battery electrolytes and additives as a function of the state of charge using GEN2 electrode materials.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

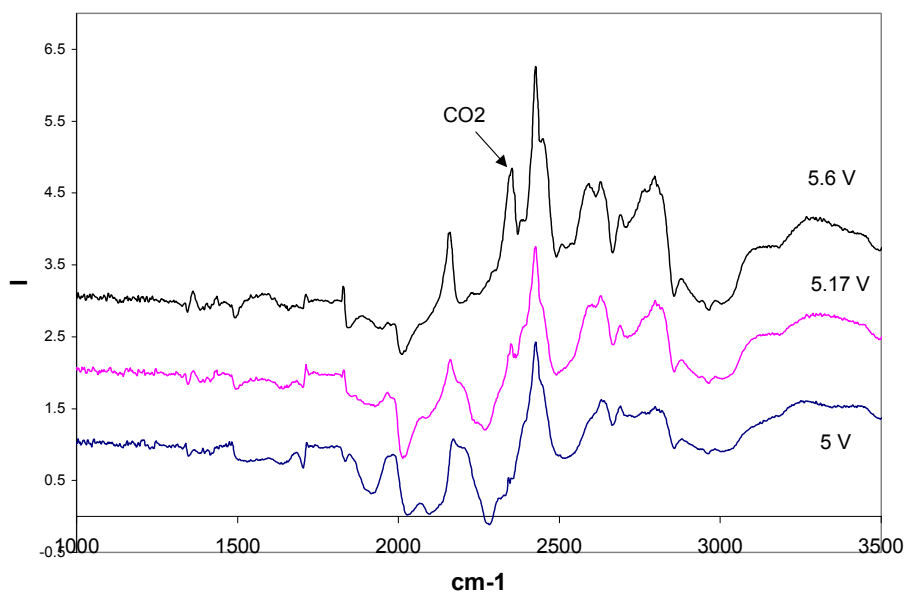
MILESTONES:

1. Determine onset potential for gas evolution from cathode materials as a function of composition of the electrolyte and the cathode material. (6/02)
2. Determine the kinetics of thermochemical reactions between the electrolyte and cathode materials as a function of temperature and composition. (9/02)

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:** It is suspected that the gassing problem in high energy Li-ion batteries is caused by electrolyte oxidation producing CO₂ among other products. We have carried out *in-situ* electrochemical oxidation studies of the common electrolyte EC/DMC-LiPF₆. The IR cell has a CaF₂ window, a glassy carbon working electrode, and lithium metal as both counter and reference electrode. The cell is assembled in the dry box and transferred to the IR spectrometer sealed from air. FTIR spectra were obtained as a function of potential. The spectra are dominated by electrolyte features, but it was clear that a CO₂ peak begins to appear above ca. 5 V. Subtractive normalized Fourier transform infrared (SNFTIR) spectra are shown in Fig. 1 using the spectrum at 4 V as the reference spectrum. Besides CO₂, it is not clear what the other features in the SNFTIR spectra arise from. The result is consistent with our previous observation using purely electrochemical (cyclic voltammetry) experiments (with the same electrolyte but Pt as working electrode) where the anodic current onset potential was observed to be about 5.2 V. The DFT predicted potential is 5.58 V. DFT also predicts CO₂ as the major product. The relationship between the amount of CO₂ produced and its IR absorption intensity will be studied next. In addition, a lower solvent oxidation potential is generally reported when metal oxides are used. Further investigation of solvent electrochemical oxidation will be carried out on cathode samples with a metal oxide thin film.
- **Accomplishments toward milestone 2 during last quarter:** Electrochemical oxidation of solvents, however, may not be the only route to produce gas in Li-ion batteries. Our TGA study on a cathode sample from a GEN2 cycled cell indicated that a significant (>6%) weight loss occurs over a temperature range from about 60 to 110°C. Therefore, it is likely that both electrochemical oxidation as well as thermo-chemical decomposition lead to gas generation in batteries. In order to understand the gassing mechanisms in relation to temperature, and shed light on battery gassing problems, we propose to use a TGA-IR system to perform real-time analysis and identify the gases produced at different temperatures. However, the TGA is not now equipped with a gas analyzer, and these experiments cannot be done at this time.

SNIFTIR Spectra for the oxidation of EC/DMC-LiPF₆



TASK STATUS REPORT

PI, INSTITUTION: E.J. Cairns, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Synthesis and Characterization of Electrodes

SYSTEMS: Li-ion and Li-polymer batteries

BARRIER: Rapid capacity fade

OBJECTIVES: The primary objectives are (1) to directly observe Li in BATT Program cathode materials, characterize the Li atomic and electronic local environment, and determine changes in this environment with cycling.

APPROACH: Our approach is to use ^7Li MAS-NMR to characterize electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. NMR data on model failure mechanisms will be used to interpret the spectra.

STATUS, OCT. 1, 2001: We compared ^7Li MAS NMR spectra for stoichiometric and substituted tunnel-structure manganese oxides after electrochemical cycling. This information helps to elucidate the structural changes accompanying capacity fade. We initiated NMR analysis of fresh LiFePO_4 -based materials, and began long-term cycling experiments on these materials.

EXPECTED STATUS SEPT. 30, 2002: We expect to have compared ^7Li MAS NMR spectra for a range of $\text{Li}(\text{Mn,Fe})\text{PO}_4$ materials and Gen2 electrodes at various states of charge. Cycled tunnel-structure materials will have been examined by MAS NMR for structural changes. The results will be helpful in interpretation of NMR spectra of cycled electrodes.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are to (1) Compare NMR-observable properties of baseline and novel electrodes, 9/02, (2) Measure capacities, capacity fading in our synthesized intermetallics, 6/02, (3) Use NMR to determine structural changes that cause capacity fade, 8/02.

PROGRESS TOWARDS MILESTONES

- **Accomplishments toward milestones during last quarter:**

^7Li MAS NMR spectra have been obtained for a variety of LiFePO_4 -based materials and Gen2 electrodes. We have determined the NMR shift and linebroadening mechanisms for LiFePO_4 -based materials, thus securing the necessary information to provide sophisticated analysis of NMR spectra of mixed $\text{Li}(\text{Mn},\text{Fe})\text{PO}_4$ materials. We have obtained spectra of Gen2 electrodes after various electrochemical tests. The results suggest that electrodes, which experience the greatest electrochemical degradation, tend to remain in a partially charged state at the end of discharge (and cell disassembly). This is probably due to SEI film formation during cycling. We are developing a NMR technique for quantifying the state of charge of an oxide electrode that is accurate to $\sim 5\%$. This technique involves digesting 20 mg of the electrode in acidic solution, and using NMR to quantify the amount of Li extracted into the solution.

Using variable-temperature NMR, we have determined that the NMR shift mechanism for LiFePO_4 -based materials is a hyperfine coupling of the ^7Li nucleus to unpaired Fe-site d electrons. Variable-field measurements suggest that the dominant linebroadening mechanism is chemical shift dispersion. This information will form the foundation for interpretation of NMR spectra of fresh and cycled $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ materials.

NMR spectra of Gen2 electrodes have been obtained after electrochemical cycling according to various protocols. Representative spectra are shown below.

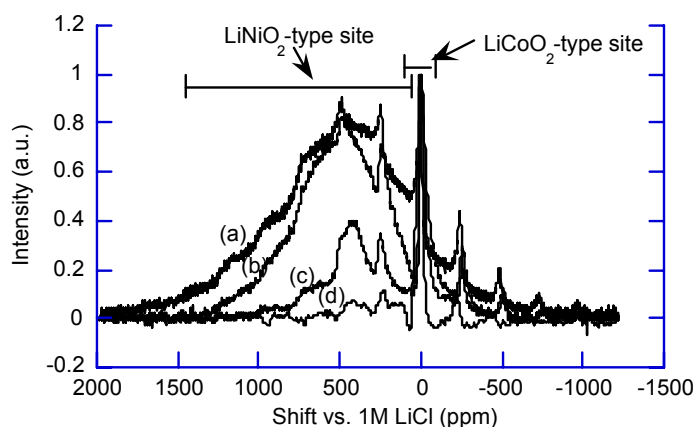


Figure 1. ^7Li MAS NMR spectra of Gen2 electrodes ($\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$). Successive damage results in less-complete Li occupation of the LiNiO_2 -type site. (a) Fresh electrode, (b) cycled once #1116, (c) stored, lost 24% power #A212, (d) cycled 140 times, lost substantial capacity #PG13.

- **Further plans to meet or exceed milestones:**

- NMR spectra of $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ materials will be obtained at various states of charge and after electrochemical cycling
- We will continue to obtain and analyze the NMR spectra of BATT program electrodes in order to elucidate failure mechanisms and design improved electrode materials.

Completion of Milestone on Intermetallic Anode Materials

The *in situ* x-ray diffraction system has been successfully constructed and tested. A family of nineteen *in situ* scans during galvanostatic Li insertion into magnesium silicide have been gathered. Each scan was collected for fifteen minutes. A phase transition is clearly observable during Li insertion as the magnesium silicide (220) peak at 40° decreases in intensity while a peak for Li_2MgSi grows in near 39.5° during Li insertion. This is a very sensitive and informative technique for tracking the formation of new phases as electrode materials are cycled. This completes the milestone (#2) and task on intermetallic anode materials.

BATT TASK 6 MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Poor polymer transport properties, side reactions, dendrite formation

OBJECTIVES: Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Use galvanostatic polarization technique to measure a complete set of transport properties, which aids selection of improved polymer electrolytes. Develop molecular dynamics program to predict diffusion coefficients in multicomponent solutions. Use simulations and experiments to explore role of SEI layer in capacity fade in alloy and insertion electrodes. Develop model of factors affecting dendrite formation on Li metal. Use Raman spectroscopy to measure *in situ* concentration profile and dendrite growth.

STATUS OCT. 1, 2001: Measurements of the transport properties of PEMO-LiTFSI and refinement of both the galvanostatic polarization method and the transition-time verification method are completed. Modification of the molecular dynamics program to predict diffusion coefficients in multicomponent electrolytes, such as LiPF_6 in EC:PC, is ongoing. Measurements of the entropy of reaction in BATT baseline electrode materials is completed. Modeling of the SEI layer is ongoing. Diagnostic experiments of the SEI layer on lithium-tin electrodes are completed. Refinement of a model of dendrite growth to include mechanical stress and surface tension is ongoing, as is experimental work to observe dendrite growth and electrolyte concentration profiles using confocal Raman spectroscopy.

EXPECTED STATUS SEPT. 30, 2002: Analysis of the effect of side reactions on measurements of transport properties will be completed. Molecular dynamics simulations of diffusion coefficients will be completed. Modeling of the SEI layer will be ongoing. Inclusion of mechanical properties in the model of dendrite growth will be completed, and further refinements to the model will be ongoing. *In situ* confocal Raman spectroscopy measurements of dendrite growth and concentration profiles will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES:

1. Model of the effect of side reactions on transport property measurements by Jan. 1, 2002.
2. Molecular dynamics simulation of LiPF_6 in carbonate solvents by Sept. 1, 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone 1 during last quarter:** Completed. While it is generally believed that Li metal is protected by the SEI layer from continuous reaction with the electrolyte, there is evidence that the SEI layer in some electrolytes, such as those containing the LiTFSI salt, allows continuous (albeit inhibited) reaction of the Li metal with the electrolyte. A slow side reaction, with a reduction potential only a few tens of millivolts positive to that of Li metal, at the Li electrode in PEO-LiTFSI polymer electrolyte, apparent through transition-time polarization curves in dilute (<0.5 mol/L) solutions, was incorporated into a model of symmetric cells employing Li electrodes. By simulating the electrochemical experiments involved in obtaining transference numbers, diffusion coefficients, and activity coefficients (galvanostatic polarization, restricted diffusion, and concentration-cell open-circuit potential (OCP)) as well as transition times, the side reaction was shown to be capable of introducing error into the calculation of cationic transference numbers at low concentrations. The solvent-reduction reaction makes the calculated cationic transference number lower (even to negative values) than its true value. This effect is primarily exerted through an alteration of surface concentrations in the concentration-cell OCP experiment. The side reaction increases the concentration of Li ions in the low-concentration polymer adjacent to the working electrode, thereby increasing the potential of that electrode with respect to the counterelectrode at the reference electrolyte concentration, and introducing error into measurements of the variation in potential with apparent electrolyte concentration. Activity coefficient measurements also rely on this calibration curve and would be affected, while diffusion coefficient measurements are essentially unaffected because of the low and nearly equal rates of the side reaction on the two Li electrodes.

- **Accomplishments toward milestone 2 during last quarter:** Diffusion coefficients have been calculated using the molecular dynamics simulation and are in qualitative agreement with experimental values for LiPF_6 in propylene carbonate and dimethyl carbonate/ethyl-methyl carbonate mixtures. We will be refining the parameters used to describe interatomic attraction and repulsion in order to attempt quantitative agreement and to examine the molecular basis for conductivity and diffusion in liquid electrolytes for Li batteries.

Other Progress

We characterized the SEI layer on lithium-tin electrodes in propylene carbonate (PC) with 1 M LiClO_4 electrolyte, and found that it is similar to that formed on glassy carbon, since the reduction potential for PC (~ 1 V) is so much higher than the potential of lithium-tin (0.38 to 0.76 V). PC reduction begins above 0.8 V and consumes at least 60 mAh/g Sn of irreversible capacity. The interfacial impedance varies considerably with potential. FTIR shows that the surface of the SEI layer formed in PC contains lithium-alkyl carbonates.

We have developed a model for dendrite growth to evaluate the effects of various parameters on the dendrite growth rate. Analysis of interfacial forces has shown that the elastic properties of the separator control dendrite growth rate as much or more than surface forces during the early stages of growth. We have modified the model to include a more accurate sinusoidal perturbation to the Li surface. The polymer is currently modeled as a Hookean solid. Future work will explore the effects of viscoelasticity in the polymer on dendrite growth.

Refinements to the model of ion and electron transport through the SEI layer are ongoing.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan

TASK TITLE - PROJECT: Modeling - Failure Mechanisms in Li-ion Systems: Design of Materials for High Conductivity and Resistance to Delamination

SYSTEMS: Low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective of these studies is to explain and predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Correlation of delamination, high impedance and temperature/structure/function phenomena with specific materials composition and morphology will be developed, making use of the extensive software developed for tracking mechanical and conductive losses in heterogeneous materials at UM. Specific comparisons will be undertaken, using cells provided by the ATD and BATT programs.

STATUS OCT. 1, 2001: We developed finite element representations of model carbon materials, and developed a means for measuring conductivity of thin electrodes.

EXPECTED STATUS SEPT. 30, 2002: We expect to confirm structure/function relationships in ATD Gen 1 and Gen 2 cells, through image analysis and testing, with verification from finite element simulations.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: We expect to test DOE ATD Program Gen 1 and 2 cells, provided by Argonne National Laboratories, by May 31, 2002.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestone over last quarter**

We have completed conductivity testing and initiated image analysis of materials from three laboratories participating in DOE-sponsored efforts: Argonne National Laboratory (Dr. Gary Henriksen, contact), Lawrence Berkeley National Laboratory (Dr. K. Kinoshita, contact), and the Institut de Recherche d'Hydro-Québec (Dr. Karim Zaghib, contact). Anode (LBNL, IREQ) and cathode (ANL) materials have been tested.

We have worked extensively in this period to understand large variations in experimental results using several techniques for conduction mapping. We have concentrated efforts on closed-form solutions of interacting conductive fields, in order to design more sensitive experiments. We have also continued to expand our simulations capability for multiphase materials. Our efforts can be summarized in this project period as follows:

1. experimental conductivity mapping of materials provided by three DOE-sponsored laboratories, has continued, using both two-probe and four-probe conduction experiments, with various tip geometries and spacings
2. mathematical design of experiments, to design improved conduction experiments
3. conductivity code development for automatic generation of irregular arrays of conductive particles with verification of recently added features to handle boundary effects and irregular particle connections
4. extension of mechanics modeling of more complex fiber interconnects, allowing 3D results to be used to implement revised mechanics assumptions in faster, more efficient 2D simulations, and also developing correlations between real material behavior and model behavior

- **Further plans to meet or exceed milestone**

We have requested more materials of LBNL for collaborative purposes. We have also continued work on materials supplied by IREQ. Our conduction and mechanics simulations have advanced in the project period, and we have also completed a set of calculations on improved design of conduction experiments.

- **Reason for changes from original milestone:** N/A

PROPOSALS UNDER REVIEW

ORGANIZATION <i>(Principal Investigator)</i>	TITLE	STATUS
University of Michigan <i>(A. Matzger/G.A. Nazri)</i>	Optimization of Li Ion Transport in Polymeric Electrolytes: A Theoretical and Experimental Approach	Request for Proposal - Rejected
Clemson University <i>(D. DesMarteau)</i>	New Battery Electrolytes Based on Oligomeric Lithium bis(perfluoroalkyl) imide Salts	Request for Proposal - Contract Placed
EIC Laboratories, Inc. <i>(G.L. Holleck)</i>	Applied Research on Novel Electrolytes for Advanced Rechargeable Lithium Batteries	Request for Proposal - Rejected
Pennsylvania State University <i>(H.R. Allcock)</i>	Optimization of SPE Battery Performance Through the Development of Novel Electrolytes and Cathodes	Request for Proposal - Rejected
University of Minnesota <i>(W.H. Smyrl/B.B. Owens)</i>	Novel Solid Polymer Electrolyte Systems	Request for Proposal - Rejected
University of South Carolina <i>(P.B. Balbuena)</i>	Modeling of Salt Chemistry in Li-Ion Battery Electrolytes	Request for Proposal - Rejected
University of Utah <i>(G.D. Smith)</i>	A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Li Cations in Polyether-Based SPEs	Request for Proposal - Under Negotiation
Covalent Associates <i>(A.B. McEwen)</i>	Ionic Liquid Electrolyte Safety Determination and Optimization	Request for Proposal - Rejected
University of Michigan <i>(M.D. Curtis/G.A. Nazri)</i>	New Single-Ion Electrolytes for Li-Ion Battery Technology	Request for Proposal - Rejected
University of Texas at Austin <i>(J.B. Goodenough)</i>	Cathodes - Novel Materials	Unsolicited Under Review
North Carolina State Univ. <i>(S.A. Khan)</i>	Composite Polymer Electrolytes for Use in Lithium and Lithium-Ion Batteries	Renewal Under Review

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)
QUARTERLY REPORT FOR OCTOBER – DECEMBER 2001
CALENDAR OF UPCOMING EVENTS

December 2001

- 11 - 14 The EVAA Electric Transportation Industry Conference & Exposition 2001–
Sacramento, CA (Registration Headquarters, 499 Seaport Court, Suite 300, Port of
Redwood, CA 94063; 800-260-8972, fax: 650-369-0618;
information@connectionsww.com; <http://www.evaa.org>)

May 2002

- 12 - 17 201st Electrochemical Society Meeting – Philadelphia, PA – ECS Centennial Meeting
(The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896;
(609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org)

June 2002

- 23 – 28 11th International Conference on Lithium Batteries (IMLB-11) – Monterey CA (IMLB
11 Conference Secretariat, c/o The Electrochemical Society Inc., 10 South Main Street,
Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743;
ecs@electrochem.org; <http://www.electrochem.org/meetings/011/imlb11.html>)

July 2002

- 14 – 19 EESAT 2002 - International Ceramics Congress - Materials for Electrochemical,
Chemical, Nuclear and Environmental Applications – Florence Italy (Dr. Nancy Clark,
Sandia National Laboratories, P.O. Box 5800, MS 0613, Albuquerque NM 87185;
nhclark@sandia.gov; <http://www.dinamica.it/cimtec>)

September 2002

- 3 - 8 53rd ISE – Dusseldorf, Germany (Prof. J.W. Schultze, Institut für Physikalische Chemie
II, Universität Dusseldorf, Universitätsstr 1, D-4000 Dusseldorf 1, Germany; fax: 49
2118112803; schultzj@rz.uni-duesseldorf.de)

October 2002

- 15 - 18 17th International Electric Vehicle Symposium & Exposition – Montreal, Canada (Ms.
Pam Turner, EVS-17 Symposium Manager; (650) 365-2802; fax: (650) 365-2687;
electricevent17@aol.com).
- 6 - 11 202nd Electrochemical Society Meeting – Salt Lake City, UT (The Electrochemical
Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax:
(609) 737-2743; ecs@electrochem.org)

August 2003

- 31 – Sept. 5 54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

September 2004

- 55th ISE – Thessaloniki, Greece (Prof. E. Theodoridou)